

²⁰
29. The method of claim ¹⁹~~28~~ wherein said mixture of steam and hydrocarbon comprises water and methane.

A1 ²¹
30. The method of claim ²⁰~~29~~ wherein said mixture of steam and hydrocarbon consists of water and methane. --

REMARKS

Claims 1-9 are pending. By the foregoing amendment, claims 1-9 have been canceled without prejudice or disclaimer. Claims 10-30 have been added. New claim 10 is modeled closely on original claim 1 and new claim 20 is modeled closely on original claim 4. Additional description has been provided to clarify the claims. Support for the new claims can be found in Fig. 1 (claim 10), Fig. 2 (claim 20), and elsewhere in this relatively brief specification. The new claims have been added to improve clarity of the claims - the independent claims do not contain added limitations to distinguish over the cited art - as can be seen from the discussion below, the cited art does not render obvious the claims either in their original, or their more clear revised form.

L Applicants have discovered that steam reforming reactions utilizing short residence times and a spinel support have unexpectedly long stability, high conversion and good selectivity.

Rejections Under 35 U.S.C. §112

The claims had been rejected on the grounds that: the claims did not explain the conditions for the comparison; they contained an anonymous hydrocarbon and an anonymous spinel; the term "forming" was unclear; and the term "maintaining activity" was unclear.

The claims have been rewritten in a new format based on the results illustrated in Figs. 1 and 2. The terms "forming" and "maintaining activity" are no longer present in the claims. The newly added dependent claims include additional limitations that further define the invention.

Applicants respectfully traverse the rejection with regard to the terms "hydrocarbon" and "spinel." The applicability of steam reforming to a wide variety of hydrocarbons has long been known. For example, Rostrup-Nielsen in the text "Steam Reforming Catalysts" describes some work from the 1800's on steam reforming with various hydrocarbons (see attached pages 26-27). Rostrup-Nielsen also describes his own research with various hydrocarbons (see attached pages 113-115 and 119-120).

Additionally, applicants have shown that their method is applicable to a variety of hydrocarbons. See attached Declaration by Dr. Yong Wang. As shown in the Declaration, the inventive method has been found to produce conversions of 60% or greater and CO selectivities of 62% or less for each of the hydrocarbons: methane, butane, isooctane, synthetic crude, gasoline, diesel, and JP-8.

In view of the knowledge in the art of the broad applicability of steam reforming to a wide variety of hydrocarbons and in view of applicants' showing of better than the claimed effectiveness for methane, butane, isooctane, synthetic crude, gasoline, diesel, and JP-8, it is clear that the claimed

method will operate with a wide variety of hydrocarbons. It is possible that some hydrocarbons could be identified that would not achieve the claimed results; however, that possibility is not a proper basis for a section 112, first paragraph rejection. "It is not a function of the claims to specifically exclude either possible inoperative substances or ineffective reactant proportions." *In re Dinh-Nguyen*, 181 USPQ 46, 48 (CCPA 1974). See also *In re Angstadt*, 190 USPQ 214, 218-219 (CCPA 1976) and *Ex parte Calingaert*, 52 USPQ 263, 264 (Pat. Off. Bd. of App. 1942). Since applicants have shown that the claimed method operates with a variety of hydrocarbons, and since the suitability of virtually any hydrocarbon could be tested by routine experimentation, the term "hydrocarbon" complies with the requirements of section 112, first paragraph, and withdrawal of this rejection is respectfully requested.

The term "spinel" is similarly in compliance with the requirements of section 112, first paragraph. Spinel is defined to a specific class of materials having very similar composition and the same structure. See attached copies from Wells, "Structural Inorganic Chemistry," 5th ed. 1987 pp. 592-596, 318.5. Given the great compositional and structural similarity of spinels, it would be expected that they would perform similarly. Furthermore, as pointed out in the cases cited above, it is not a function of the claims to exclude all possible inoperative substances. Accordingly, the term "spinel" complies with the requirements of section 112, first paragraph, and withdrawal of this rejection is respectfully requested.

Rejection Under 35 U.S.C. §103

The Examiner has acknowledged that the cited references fail to disclose the claimed residence time. However, the Examiner states that it would have been within the discretion of the artisan to select reaction conditions for the sole purpose of minimizing the residence time and has cited case law suggesting that the motivation for reducing residence time is to reduce costs. This rejection is traversed on two independent grounds (1) the cited references do not establish a *prima facie* case of obviousness because there was not a proper motivation for modifying the cited references, and (2) even if there were a proper a *prima facie* case of obviousness, applicants have found unexpected results that establish nonobviousness of the claimed method.

The fact that the prior art could be modified to reduce residence times is not a sufficient basis for establishing a *prima facie* case of obviousness. See, e.g., *In re Mills*, 16 USPQ2d 1430, 1432 (Fed. Cir. 1990) “the mere fact that the prior art could be modified would not have made the modification obvious unless the prior art suggested the desirability of the modification.” In this case, the cited prior art did not suggest the desirability of the modification. In particular, there is no suggestion in the cited references that reducing residence time below 0.1 seconds would be economically advantageous, and the prior art did not suggest that there would have been an economic motivation to reduce residence times. To the contrary, based upon the prior art, one skilled in the art would have expected reduced residence times to reduce conversion and worsen selectivity - these are economically *undesirable* results. Therefore, there is not a *prima facie* case of obviousness and withdrawal of the rejection is respectfully requested.

Even if the cited references did establish a *prima facie* case of obviousness, the claimed invention would still be patentable because applicants have found unexpected results that establish nonobviousness of the claimed method. Applicants have discovered that steam reforming reactions over a spinel-supported catalyst, when conducted at residence times of less than about 0.1 seconds, produce high conversion and good selectivity while maintaining an active catalyst. These superior results were not expected in the prior art.

Accordingly, withdrawal of the rejection under 35 U.S.C. §103 is respectfully requested.

Conclusion

If the Examiner has any questions or would like to speak to Applicants' representative, the Examiner is encouraged to call Applicants' attorney at the number provided below.

Respectfully submitted,

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STEAM REFORMING CATALYSTS

AN INVESTIGATION OF
CATALYSTS FOR TUBULAR
STEAM REFORMING
OF HYDROCARBONS



BY
JENS R. ROSTRUP-NIELSEN

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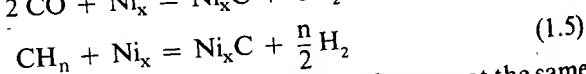
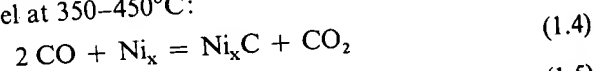
1.2 Historical and Future Aspects.

1.2.1 Early Work

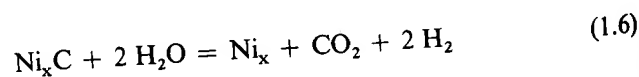
The catalytic interaction between hydrocarbons and metals was already observed in 1817 by Davy^{69, 209} during his famous experiments with the wire-gauze safety-lamp. When a hot platinum or palladium wire was exposed to mixtures of air and hydrogen or "olefiant gas" (ethylene), a flameless combustion was observed. "The same circumstances occurred with certain inflammable vapours. I have tried those of ether, alcohol, oil of turpentine and *naphtha*". Davy also observed that "a thin film of carbonaceous matter destroys the igniting power of platinum, and a slight coating of sulphuret deprives palladium of this property". It will be shown later than the problems of coking and sulphur poisoning are some of the major problems in steam reforming of *naphtha*.

Some years later Gilbert⁹⁷ described the use of nickel for the inflammable combustion. In a paper from 1834⁸⁷ Faraday emphasized the importance of "perfectly clean and metallic surface" for the catalytic reaction between hydrogen and oxygen. Again, poisoning effects were caused by a carbonaceous film formed in the presence of olefiant gas (ethylene) or by sulphur compounds. The interaction between olefins (*ölbildende Gase*) and nickel was reported in 1842 by Marchand¹⁶³, who observed the formation of a carbon layer containing a few percent of metallic nickel.

A process for conversion of hydrocarbons into hydrogen in the presence of steam was described by Tessie du Motay and Marechal in 1868²⁵³. The hydrocarbons and steam were passed over calcium oxide resulting in formation of calcium carbonate and hydrogen. The application of nickel for this process was claimed in 1889 by Mond and Langer²⁸⁸. In a first step carbon monoxide or hydrocarbons were decomposed over nickel at 350–450°C:



A second step involved oxidation of the carbide with steam at the same temperatures:



The decomposition of carbon monoxide and methane over nickel is the subject of part of the present study.

At the same time, Lang¹⁴⁷ studied the homogeneous reaction between steam and methane. The experiments, which were performed at a molar ratio $\text{H}_2\text{O}/\text{CH}_4$ of unity, resulted in very small conversions even at 950–1050°C. Moreover, the reaction was accompanied by formation of coke. In 1902, Sabatier and Senderens²²³ found that the reverse reaction, i.e. hydrogenation of carbon monoxide and dioxide to methane, was catalyzed effectively by nickel. Apparently, Sabatier showed minor interest in the reforming reaction, and although some industrial interest was reflected by patents of Dieffenbach and Moldenhauer in 1909²⁸⁹ and by BASF (Mittasch and Schneider) in 1912²⁹⁰, Sabatier did not mention steam reforming in his book²²⁴ which summarizes among other topics his comprehensive studies of reactions on nickel catalysts. The first detailed study of the catalytic reaction between steam and methane to be published is apparently that of Neumann and Jacob¹⁸⁰ from 1924. The experiments resulted in gas mixtures close to the equilibria of reactions (1.2) and (1.3).

Shortly after, an increasing interest developed in utilizing the reforming reactions for industrial conversion of natural gas or methane-rich gases into synthesis gas or hydrogen^{88, 155}. This resulted in numerous patents issued around 1930⁹⁰ among which one²⁹² described a process where the catalyst was placed in externally heated tubes of alloy steel. A broad range of catalyst compositions was claimed as for example²⁹¹ "catalysts consisting of iron, nickel or cobalt activated by the addition of other metals or metallic compounds. . . . As activating agents, metals whose oxides are reducible with difficulty, or compounds thereof, are especially useful, e.g. chromium, vanadium, and compounds of alkali, alkaline earth, and earth metals, such as potassium, magnesium, and aluminum. . . ." or more simply²⁹³ "a substance comprising a metal of the iron group with an activating addition of a non-reducible oxide of a metal from groups 2 to 6 of the periodic system".

1.2.2 Industrial Developments

The first industrial steam reformer was installed at Baton Rouge by Standard Oil of New Jersey⁵² and started in 1930. Six years later the first I.C.I.-steam reformer was commissioned at Billingham⁹⁴. The reforming

TABLE 5-10 Reforming at Elevated Pressure
Experiments with Various Hydrocarbons. Catalyst A18 (0.5 g as 1-2 mm Particles)
Temperature 500°C, Pressure 31 atm abs, $H_2O/H_2 = 10$

Exp. No.	Feed	H_2O/C mol atom	P_{C,H_m} atm	Space Velocity g-atom kg cat. · h $\times 22.4 \cdot 10^{-3}$	Conver- sion to CO, CO ₂ , CH ₄ %	k_a calc. from eq. (5.11) g-atom/g/h	k_a \times no C-atoms no C-C bonds	k_a \times P_{CH_4} $P_{C_{2H_6}}$
1211	methane	3.71	6.0	194	4.65 ^a	0.43	—	0.43
1212	ethane	3.79	3.3	207	31.5	3.5	1.8	6.4
1230	ethane	3.85	3.2	204	22.5	2.3	1.2	4.3
1216	(<i>n</i>)-butane	3.85	1.7	204	39.9	4.6	3.5	16
1210	cyclohexane	3.73	1.2	209	53.9	7.2	7.2	36
1208	benzene	3.96	1.1	200	5.7	0.53	0.53	2.9
1209	<i>n</i> -heptane	3.83	1.0	206	18.7	1.9	1.6	11
1214	tri-methyl-butane	3.88	1.0	201	33.2	3.6	3.1	22
1213	<i>n</i> -decane	3.77	0.7	104	32.8	1.9	1.7	16
1203	naphtha 36 (FBP 120°C)	3.74	—	209	40.0	4.8	—	—
1215	naphtha 36 (FBP 120°C)	3.76	—	209	35.8	4.1	—	—
1207	naphtha 49 (FBP 169°C)	3.69	—	212	15.5	1.6	—	—

^a) Conversion to CO and CO₂

No.	CH ₄ : 0.01 vol. %	b) calculated from gas analyses									
		0.01	0.72	0.02	0.38	86.40	87.71	0.01	5.14	5.21	7.02
<i>n</i> -C ₇			0.18	0.07	0.17	8.45	7.67	98.78	5.45	4.78	5.50
<i>iso</i> -C ₇			0.01		0.11	1.72	1.52		1.53	4.31	3.06
DMCP											
MCH (+ 22 DMH + 113 TMCP)	0.01	0.06			0.35	0.72	0.69		1.72	6.66	5.49
ECP (+ 25 DMH)		0.01			0.11	0.19	0.18		0.52	1.04	1.15
Toluene		0.03			0.38	0.37	0.36		1.76	1.82	2.70
<i>n</i> -C ₈			0.06	0.07	3.26	0.31	0.35		1.02	6.40	7.16
<i>iso</i> -C ₈ + C ₈ +					3.30	0.20	0.19		2.33	11.87	14.60
ECH					0.82				0.09	2.53	1.74
Ethylbenz					0.54				0.12	0.30	1.10
Xylenes					3.00				0.33	4.36	4.48
<i>n</i> -C ₉					5.06				0.37	4.60	5.02
C ₉ +					10.26				0.17	10.43	15.41
<i>n</i> -C ₁₀			1.61					> 95	0.06	0.18	1.43
C ₁₀ +			7.02						0.07	2.07	9.62
<i>n</i> -C ₁₁					0.09						0.06
C ₁₁ +					1.09						1.10

a) CH₄: 0.01 vol. %

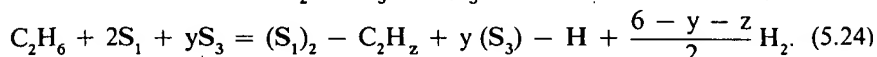
b) calculated from gas analyses

c) Naphtha No.	36	49
ASTM: IBP/MBP/FBP (°C)	40 65 120	40 89 169
Spec. grav. (g/ml)	0.674	0.705

This expression may explain the kinetic coefficients obtained for catalyst A1 as shown in (5.13), and that the kinetic coefficient for steam may become less than -1 as observed for catalysts A35 and B4, but the reaction orders with respect to steam and hydrogen are not numerically equal as predicted.

In addition, the over-all pressure coefficients to be deduced from Fig. 5-12 correlate with the kinetic order for steam indicating the rôle of hydrogen to be more complicated than accounted for in the simple sequence.

In Boudart's⁴² recent kinetic interpretation of ethane hydrogenolysis, hydrogen is assumed to be in a chemisorption equilibrium with nearby saturated sites on the metal surface different from the sites where the hydrocarbon reacts. If so, step (5.14) should be reformulated by:



This implies that the term $p_{\text{C}_2\text{H}_6}$ in (5.21) and (5.22) should be replaced by $p_{\text{C}_2\text{H}_6}/p_{\text{H}_2}^{y/2}$. Hence:

$$r = \frac{k_A \cdot p_{\text{C}_2\text{H}_6}/p_{\text{H}_2}^{y/2}}{(1 + (2k_A/k_r)(1/K_w)(p_{\text{C}_2\text{H}_6}/p_{\text{H}_2\text{O}})p_{\text{H}_2}^{1-y/2} + K_w(p_{\text{H}_2\text{O}}/p_{\text{H}_2}))^2} \quad (5.25)$$

$$r = k \cdot p_{\text{C}_2\text{H}_6}^{1-2n} \cdot p_{\text{H}_2\text{O}}^{2(n-m)} \cdot p_{\text{H}_2}^{2(m-n)+y(n-\frac{1}{2})} \quad (5.26)$$

It is shown in Chapter 7 (p.173) that the sequence for ethane reforming in principle can easily be extended to an arbitrary n -paraffin. An expression equivalent to (5.25) can be derived.

5.4.1.2 Reforming of Various Hydrocarbons

The simple sequence for hydrocarbon adsorption simulating the steps suggested in hydrogenolysis remains speculative and it can hardly be used for evaluation of the reactivity trend of the higher hydrocarbons because the results from hydrogenolysis have been reported mainly for temperatures below 400°C. The apparent multiple cleavage of carbon-carbon bonds and the relatively high reactivity of branched hydrocarbons

and cyclohexane deviate from the pattern generally observed in hydrogenolysis at low temperature, at which nickel attacks selectively the ends of chains^{142, 165}.

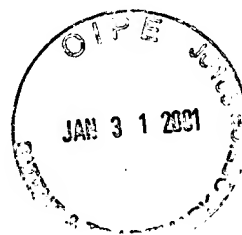
In studies of the reforming reaction in the temperature range 250–350°C Balashova, Slovokhotova, and Balandin¹⁴ found a stepwise degradation of hydrocarbons and a much higher reactivity of *n*-paraffins than of cycloparaffins. At higher temperatures, 350–450°C, Phillips, Mulhall and Turner¹⁹⁵ observed partially decomposed hydrocarbons from the reforming reaction with branched hydrocarbons which were less reactive than normal paraffins. Methyl cyclohexane was found to be slightly less reactive than *n*-heptane, and a small amount of toluene was found among the products. In the present study at 500°C, intermediates were indicated only for benzene, this being the least reactive hydrocarbon. In experiments at very high temperatures, 750–950°C, Yoshitomi, Morita and Yamamoto²⁷⁵ found cyclohexane to be more reactive than *n*-hexane above approx. 800°C. Although thermal pyrolysis must have influenced the latter results, the relative reactivities appear to vary with temperature. This conclusion is supported by the different activation energies for normal and cycloparaffins reported by Balashova, Slovokhotova and Balandin¹⁴. On a rhodium catalyst studied by Treiger *et al.*²⁵⁸ the order of reactivity of some hydrocarbons was found to differ from results obtained on a nickel catalyst.

At 600°C Schnell²³³ detected substantial amounts of low olefins in reforming experiments with propane and butane performed at very short contact times. In the present experiments on butane reforming at atmospheric pressure, conversion and contact times (approx. $2 \cdot 10^{-3}$ sec) were within the range considered by Schnell. Since no intermediates were identified in the present studied performed at 400–525°C, the olefins observed by Schnell are most probably not intermediates from the reaction on the nickel surface but products from thermal pyrolysis or cracking on the carrier material, these reactions being more pronounced at the temperature level applied by Schnell. On this basis, it appears reasonable to assume multiple cleavage of the carbon-carbon bonds on the nickel surface for most non-aromatic hydrocarbons at temperatures of 500°C and above, and to consider minor amounts of ethane, propane, and other higher hydrocarbons observed in the effluent of some tubular reformers as being hydrogenated products from pyrolysis or cracking.

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A. F. WELLS

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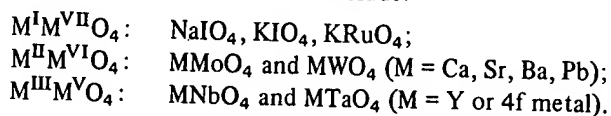
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the structure. In the distorted wolframite structure of CuWO_4 Cu has 4 O at 1.98 Å and 2 O at 2.40 Å. As in all $\text{W}^{\text{VI}}\text{O}_6$ octahedra there is a range of W—O distances from 1.76–2.2 Å.

The scheelite and fergusonite structures

The scheelite structure is named after the mineral with the composition CaWO_4 . Examples of compounds with this structure include:



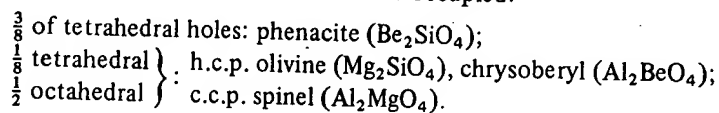
Detailed X-ray and n.d. studies of the (tetragonal) scheelite structure show very slight distortion of the WO_4 tetrahedra (four angles of 107.5° and two of 113.4° , W—O, 1.78 Å). Many compounds of the third group listed above have a distorted (monoclinic) variant of the structure (*fergusonite* structure). The oxides $\text{YTi}_{0.5}\text{Mo}_{0.5}\text{O}_4$ and $\text{YTi}_{0.5}\text{W}_{0.5}\text{O}_4$ show an interesting difference, the Mo compound having the tetragonal scheelite structure and the W compound the fergusonite structure. Such differences between compounds of Mo and W are numerous, and other examples are noted elsewhere.

A different deformed version of the scheelite structure is found for KCrO_3Cl . Replacement of 3 Ca^{2+} in the scheelite structure by 2 M^{3+} gives a 'defect scheelite' structure, $\text{M}_2\Box_3\text{WO}_4$, where \Box represents a vacancy. At least five different arrangements of the vacancies have been found in the structures of compounds such as $\text{Bi}_2(\text{WO}_4)_3$ and molybdates and tungstates of Sc, La, and 4f metals.⁽¹⁾

(1) AC 1973 B29 2074, 2433

Oxides AB_2O_4

This is a very large group of compounds, for it includes oxides and oxy-salts of three types: $\text{A}^{\text{VI}}\text{B}_2^{\text{I}}\text{O}_4$, $\text{A}^{\text{IV}}\text{B}_2^{\text{II}}\text{O}_4$, and $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{O}_4$, sometimes referred to as 6:1, 4:2, and 2:3 compounds. Three structures of this type were described in our discussion of the closest packing of equal spheres, namely, those in which certain proportions of the tetrahedral and/or octahedral holes are occupied:



Phenacite and olivine are orthosilicates, and since the present group includes all compounds $\text{B}_2(\text{AO}_4)$ containing tetrahedral AO_4 ions and ions B of various sizes it is a very large one and there are numerous structures, of which a selection is included in Table 13.9. For example, the alkali-metal tungstates have four different crystal structures:

TABLE 13.9
Crystal structures of compounds AB_2O_4

C.n. of B	4	6	8	9 and/or 10
C.n. of A				
4	Phenacite	Olivine Spinel	K_2WO_4	$\beta\text{-}K_2SO_4$
6			*	K_2NiF_4
8		$CaFe_2O_4$ $CaTi_2O_4$		

For a discussion of the crystal chemistry of compounds AB_2O_4 see, for example: IC 1968 7 1762; JSSC 1970 1 557.

* We could include here a number of structures in which rutile-like chains containing A are held together by B in positions of 6-coordination (Sr_2PbO_4 , p. 214) or 6-, 7-, and 9-coordination (Ca_2IrO_4 , ZAC 1966 347 282).

Li_2WO_4 (phenacite), Na_2WO_4 (modified spinel), K_2WO_4 (and the isostructural Rb_2WO_4), and Cs_2WO_4 ($\beta\text{-}K_2SO_4$ structure), with respectively 4-, 6-, 8-, and (9 and 10)-coordination of M^+ ions.

However, we are concerned here with complex oxides rather than oxy-salts containing well-defined oxy-ions, though the dividing line is somewhat arbitrary, as is illustrated by compounds such as Li_2BeF_4 , Zn_2GeO_4 , and $LiAlGeO_4$ with the phenacite structure and $LiNaBeF_4$, Cs_2BeF_4 , and Ba_2GeO_4 with the olivine structure.

By far the most important of the structures of Table 13.9 is the spinel structure. A recent survey shows over 130 compounds with the cubic spinel or closely related structures; some 30 of these are sulphides but most of the remainder are oxides. After the spinel structure we shall deal briefly with two other structures in which there is 6-coordination of B, namely, those of $CaFe_2O_4$ and $CaTi_2O_4$, and then with the K_2NiF_4 structure.

There is considerable interest in the high-pressure forms of oxides AB_2O_4 , for high-pressure forms of olivine (Fe, Mg) $_2SiO_4$, are believed to be important constituents of the earth's mantle. High pressure tends to convert a structure into one with higher c.n.s, that is, from top left to bottom right of Table 13.9. Examples include:

Ca_2GeO_4 : olivine \rightarrow K_2NiF_4 structure (density increase 25 per cent)

Mn_2GeO_4 : olivine \rightarrow Sr_2PbO_4 structure (density increase 18 per cent).

The normal and 'inverse' spinel structures

The spinel structure is illustrated in Fig. 7.4(a). It is most easily visualized as an octahedral framework of composition AX_2 (atacamite) which is derived from the

NaCl structure by removing alternate rows of metal ions (Fig. 4.22(b), p. 170). Additional metal ions may then be added in positions of tetrahedral coordination (Fig. 7.3(a), facing page 319). In the resulting structure each O^{2-} ion also has tetrahedral coordination, its nearest neighbours being three metal atoms of the octahedral framework and one tetrahedrally coordinated metal atom.

The crystallographic unit cell of the spinel structure contains 32 approximately cubic close-packed O atoms. (There are small departures from ideal closest packing which appear to be related to the charges on the B atoms, these atoms (ions) being in edge-sharing octahedral groups.^(1a)) For every 32 c.p. O atoms there are 32 octahedral and 64 tetrahedral interstices but in the space group of spinel there are equivalent positions for 8 atoms in tetrahedral and 16 in octahedral coordination. It was therefore natural to place the A atoms in the former and the B atoms in the latter positions. The spinels MA_2O_4 (where M is Mg, Fe, Co, Ni, Mn, or Zn) have this structure, but in certain other spinels the A and B atoms are arranged differently. In these the eight tetrahedral positions are occupied, not by the eight A atoms, but by one-half of the B atoms, the rest of which together with the A atoms are arranged at random in the 16 octahedral positions. These 'inverse' spinels are therefore conveniently formulated $B(AB)_4O_4$ to distinguish them from those of the first type, AB_2O_4 . Examples of inverse spinels include $Fe(MgFe)O_4$ and $Zn(SnZn)O_4$.

The nature of a spinel is described by a parameter λ , the fraction of B atoms in tetrahedral holes; some authors refer to the degree of inversion γ ($=2\lambda$). For a normal spinel $\lambda=0$, and for an inverse spinel $\lambda=\frac{1}{2}$. Intermediate values are found (e.g. $\frac{1}{3}$ in a random spinel), and λ is not necessarily constant for a given spinel but can in some cases be altered by appropriate heat treatment. For $NiMn_2O_4$ λ varies from 0.37 (quenched) to 0.47 (slow-cooled).^(1b) Values of λ have been determined by X-ray and neutron diffraction, by measurements of saturation magnetization, and also by i.r. measurements. In favourable cases i.r. bands due to tetrahedral AO_4 groups can be identified showing, for example, that in $Li(CrGe)O_4$ Li occupies tetrahedral positions.⁽²⁾

If there is sufficient difference between the X-ray scattering powers of the atoms A and B it is possible to determine the distribution of these atoms by the usual methods of X-ray crystallography, but in spinel itself ($MgAl_2O_4$), for example, this is not possible. However, the scattering cross-section for neutrons of Mg is appreciably greater than that of Al, and this makes it possible to show that $MgAl_2O_4$ has the normal spinel structure.⁽³⁾ Many 2:3 spinels have the normal structure, though some (including most 'ferrites') have the inverse structure, as for example $Ga(MgGa)O_4$ ($\lambda=0.42$).⁽⁴⁾ Both types of structure are found also for 4:2 spinels. Normal spinels include Fe_2GeO_4 , Co_2GeO_4 , Ni_2GeO_4 , and Mg_2GeO_4 ^(4a) (which transforms to the olivine structure at $810^\circ C$); others have the inverse structure, for example, $Zn(ZnTi)O_4$ and $Fe(FeTi)O_4$ ($\lambda=0.46$).⁽⁵⁾

The spinels of composition between $MgFe_2O_4$ and $MgAl_2O_4$, which have been studied magnetically and also by neutron diffraction,⁽⁶⁾ are of interest in this connection. $MgFe_2O_4$ has an essentially inverse structure ($\lambda \approx 0.45$), that is,

nine-tenths of the Mg^{2+} ions are in octahedral (B) sites. As Fe is replaced by Al the latter goes into B sites and forces Mg into tetrahedral (A) sites, so that there is a continuous transformation from the inverse structure of MgFe_2O_4 to the normal structure of MgAl_2O_4 .

The structures of the spinels present two interesting problems. First, why do some compounds adopt the normal and others the inverse spinel structure? Second, there are some spinels which show distortions from cubic symmetry. This is part of the more general problem of minor distortions from more symmetrical structures which was mentioned in connection with ligand field theory in Chapter 7. We deal with these points in turn.

Calculations of the lattice energy on the simple electrostatic theory, without allowance for crystal field effects, indicate that while the inverse structure should be more stable for 4:2 spinels, the preferred structure for 2:3 spinels should be the normal structure. In fact a number of the latter have the inverse structure, as shown by the (approximate) values of λ in Table 13.10. The cation distribution in spinels

TABLE 13.10
Cation distribution in 2:3 spinels (values of λ)

$\begin{matrix} \text{A}^{2+} \\ \text{B}^{3+} \end{matrix}$	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Al^{3+}	0	0	0	0	0.38	—	0
Cr^{3+}	0	0	0	0	0	0	0
Fe^{3+}	0.45	0.1	0.5	0.5	0.5	0.5	0
Mn^{3+}	—	0	—	—	—	—	0
Co^{3+}	—	—	—	0	—	—	0

has been discussed in terms of crystal field theory.⁽⁷⁾ Although values of Δ (see p. 323) appropriate to spinels are not known, estimates of these quantities may be made and from these the stabilization energies for octahedral and tetrahedral coordination obtained. The differences between these quantities, of which the former is the larger, give an indication of the preference of the ion for octahedral as opposed to tetrahedral coordination.

Excess octahedral stabilization energy (kJ mol^{-1})

Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}
0	17	31	86	64	29	54	158	95	0

Thus while Cr^{3+} and Mn^{3+} occupy octahedral sites, most 'ferrites' are inverse spinels, Fe^{3+} having no stabilization energy for octahedral sites. The only normal, or approximately normal, ferrites are those of Zn^{2+} and Mn^{2+} , divalent ions which have no octahedral stabilization energy. The only inverse 'aluminate' is the Ni^{2+} spinel,

and of the above ions Ni^{2+} has the greatest preference for octahedral coordination. Note that we are disregarding all other factors (covalent bonding and differences in normal lattice energies) when we take account only of the crystal field stabilization energies. For example, for NiAl_2O_4 a classical calculation of the lattice energy, as the sum of the electrostatic (Madelung) potential, the polarization energy, and the Born repulsion energy, shows that the normal structure would be some 105 kJ mol^{-1} more stable than the inverse one, so that the crystal field stabilization of octahedral Ni^{2+} almost compensates for this. The observed structure is in fact very close to the random one, for which $\lambda = 0.33$. The fact that Fe_3O_4 is an inverse spinel with cubic symmetry while Mn_3O_4 is a normal spinel with some tetragonal distortion (for which see p. 553) is explained by the much greater preference of Mn^{3+} than Fe^{3+} for octahedral coordination by oxygen, as shown by the stabilization energies quoted above. The simple crystal field theory is seen to be very helpful in accounting for the cation distributions in these 2:3 spinels.

The second problem concerns the departures from cubic symmetry. For example, CuFe_2O_4 is cubic at high temperatures (and at room temperature if quenched from temperatures above 760°C),⁽⁸⁾ but if cooled slowly it has tetragonal symmetry ($c:a = 1.06$ at room temperature). It is an inverse spinel with Fe^{3+} in the tetrahedral sites, and it is interesting that the FeO_4 tetrahedra are not distorted. The tetragonal symmetry appears to be due to the tetragonal distortion of the Cu^{II}O_6 octahedra (p. 324). CuCr_2O_4 is also tetragonal, but with $c:a = 0.91$.⁽⁹⁾ Here the Cu atoms are in tetrahedral sites, but the bond angles of 103° and 123° show a tendency towards square coordination, or alternatively, the tetragonal distortion (type (c) of Table 7.13, p. 323) predicted by ligand field theory. The spinels of intermediate composition, $\text{CuFe}_{2-x}\text{Cr}_x\text{O}_4$, are even more interesting.⁽¹⁰⁾ For $x = 0$ (CuFe_2O_4) there is a tetragonal distortion with $c:a = 1.06$, and for $x = 2$ (CuCr_2O_4) the structure is tetragonal with $c:a = 0.91$. Over the range $0.4 < x < 1.4$ the structure is cubic. Since for $x = 0$ the structure is almost completely inverse, and at $x = 2$ nearly normal, there is a continuous displacement of Fe by Cu in the tetrahedral sites. This is similar to the MgFe_2O_4 - MgAl_2O_4 series but with the added complication that at one end of the series there is distortion due to Cu in octahedral sites and at the other due to Cu in tetrahedral sites, the elongation of the CuO_6 octahedra leading to $c:a > 1$ and the flattening of the tetrahedra to $c:a < 1$.

(Some sulphides with structures closely related to the spinel structure are noted on p. 764.)

- | | | |
|-----------------------|-----------------------|-------------------------------------|
| (1a) AC 1974 B30 1872 | (4) AC 1966 20 761 | (7) JPCS 1957 3 318; PR 1955 98 391 |
| (1b) AC 1969 B25 2326 | (4a) AC 1977 B33 2287 | (8) AC 1956 9 1025 |
| (2) AC 1963 16 228 | (5) AC 1965 18 859 | (9) AC 1957 10 554 |
| (3) AC 1952 5 684 | (6) AC 1953 6 57 | (10) JPSJ 1956 12 1296 |

Spinel superstructures

There are many spinel-like structures containing metal atoms of more than one kind. If these are present in suitable numbers they can arrange themselves in an orderly

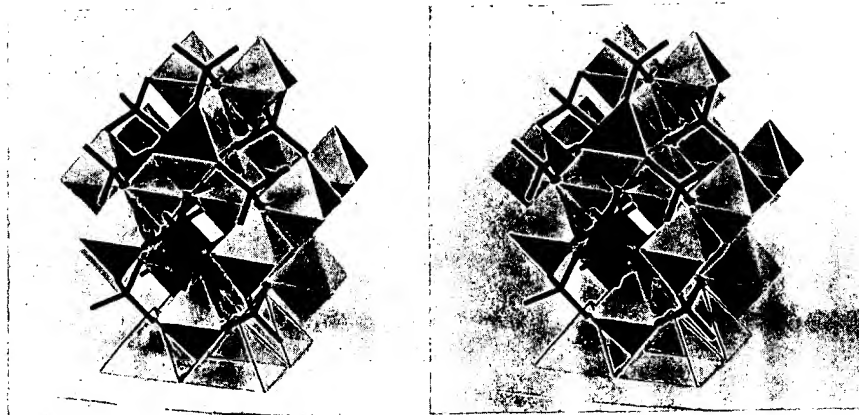


FIG. 7.3(a). The 3D octahedral framework, of composition AX_2 , is derived from the NaCl structure by removing alternate rows of metal ions as shown in Fig. 4.22(b). Although each X forms three pyramidal bonds, as in the $CdCl_2$ or CdI_2 layers, this structure is not adopted by any compound AX_2 , but it represents the idealized structure of one form of $Cu_2(OH)_3Cl$, the mineral atacamite. Additional atoms (B) in positions of tetrahedral coordination give the spinel structure for compounds A_2BX_4 . The positions of only a limited number of B atoms are indicated.

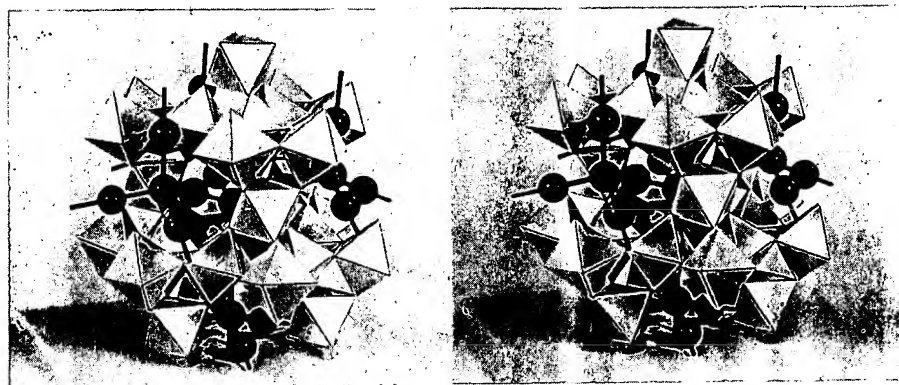


FIG. 7.3(b). The BX_6 octahedra grouped tetrahedrally around the points of the diamond net form the vertex-sharing BX_3 (B_2X_6) framework of the pyrochlore structure for compounds $A_2B_2X_6(X)$; the seventh X atom does not belong to the octahedral framework. In $Hg_2Nb_2O_7$, a framework of the cuprite (Cu_2O) type is formed by the seventh O atom and the Hg atoms, O forming tetrahedral bonds and Hg two collinear bonds.

TABLE 7.12
The simplest structures for octahedral coordination of A in compounds AX_2 and AX_3

Type of structure AX_2	Octahedra sharing	Coordination of X		Octahedra sharing	Type of structure AX_3
3D: rutile $CaCl_2$	2 edges and 6 vertices	Triangular Pyramidal	Linear Non-linear	6 vertices 6 vertices	3D: ReO_3 RhF_3
3D: atacamite* Layer (CdI_2 , $CdCl_2$)	6 edges 6 edges	Pyramidal Pyramidal	Non-linear Non-linear Non-linear	3 edges 3 edges 2 faces	3D** Layer (BiI_3 , YCl_3) Chain (ZrI_3)

* No examples known for simple halides AX_2 (Fig. 7.3(a)).

** Structures based on 3D 3-connected nets; no examples known (Fig. 7.3(c) and (d)).

be localized close to the cations, with the result that the outer surfaces of the layers are electrically neutral (Fig. 7.4(a)). In the AX_3 chain structure of Table 7.12 the chains of face-sharing octahedra are perpendicular to the planes of c.p. X atoms (Fig. 7.4(b)). The large van der Waals contribution to the lattice energy arising from the close packing of the X atoms, giving the maximum number of X-X contacts between the layers or chains, explains why there is little difference in stability between the layer and chain structures for halides AX_3 , a number of which crystallize with both types of structure ($TiCl_3$, $ZrCl_3$, $RuCl_3$).

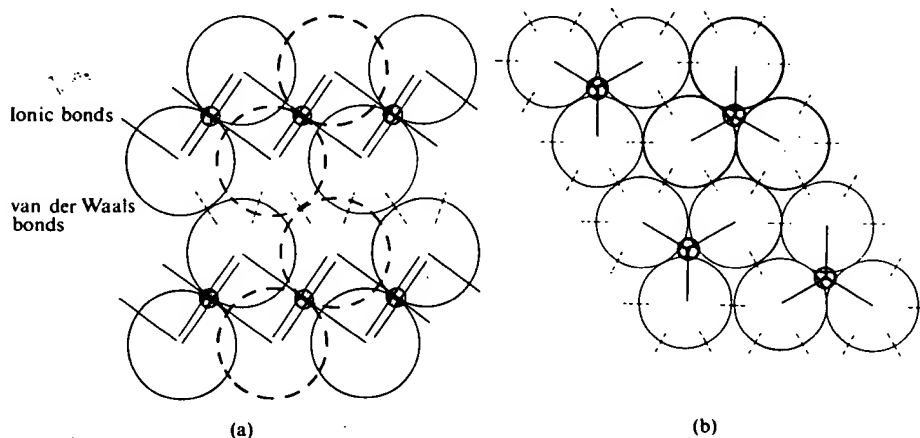


FIG. 7.4. (a) Diagrammatic elevation of AX_3 layer structure (layer perpendicular to plane of paper); (b) AX_3 chain structure viewed along direction of chains.

Limitations on coordination numbers

We have commented on the absence of structures of ionic compounds A_mX_n with coordination numbers of A greater than eight or nine. If we derive 2-dimensional